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Demixing in a Quasi-2D Surface-Frozen Layer

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A hexagonally packed solid bilayer forms at the liquid-vapor interface of long chain 1-alcohols and their mixtures by a first-order transition several °C *above* their bulk freezing point[1,2]. In mixtures, the ability to change the bulk liquid concentration allows reaching different regions in phase space and thus discovering new phases and phase transitions[3]. We have studied the surface-frozen (SF) layer of a $C_{18}OH$ (72%) + $C_{28}OH$ (28%) alcohol mixture in a saturated water vapor atmosphere by x-ray reflectivity (XR). Kiessig fringes in the XR reveal the formation of the SF bilayer at 64.5 °C. Upon cooling two regimes are found having fringes of different periods. For example, as shown in Fig. 1, the positions of the 4th minima in the two regimes differ by 0.04 $Å^{-1}$. The two regimes extend from 64.5 to 63.5 °C, and from 63.5 to bulk freezing at 62.5 °C, with SF bilayers 66.6 Å and 77.3 Å thick, respectively. The transition at 63.5 °C is abrupt, and no thickness changes are observed within each regime. The fraction of $C_{28}OH$ in the surface frozen phase is, usually, significantly different from its concentration in the liquid bulk phase. While in the liquid bulk $C_{18}OH$ and $C_{28}OH$ mix well, the big mismatch in the chain lengths should prevent mixing in the solid surface phase at low temperatures. A comparison of our results with previous measurements on the pure components[1] indeed shows that the high temperature surface bilayer phase is a mixture having ~0.7 molar fraction of $C_{18}OH$, while the lower temperature surface phase is a pure $C_{28}OH$ bilayer. The demixing transition observed here is a rare case of a 2D demixing transition in a solid, probably made kinetically possible only by the bilayer being able to easily exchange molecules with the nearby underlying 3D bulk liquid.

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References:

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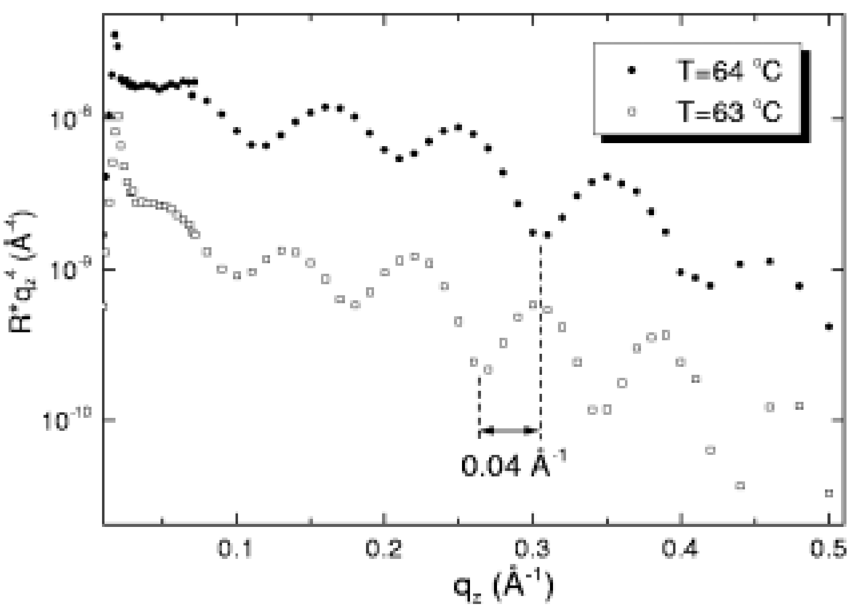

Fig. 1: Reflectivity for the high and the low temperature phases of the surface-frozen bilayer, multiplied by q_z^4. The low-temperature phase reflectivity is downshifted for clarity.